Status and Challenge of Chemically Amplified Resists for Extreme Ultraviolet Lithography

1. Status and challenge
2. Anion-bound resist
3. Wavelength diffusion

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ITRS2010 Update

Lithography roadmap

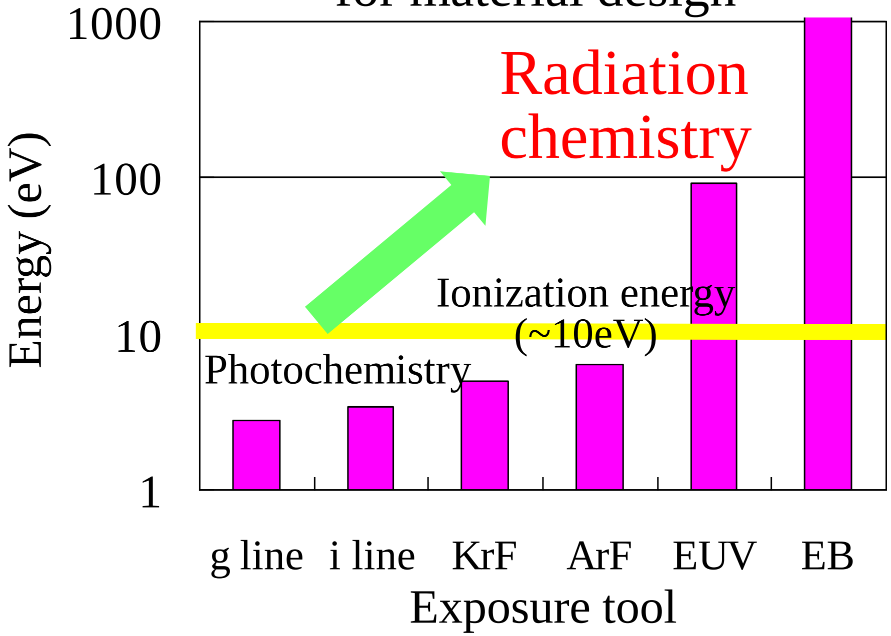
Year	2001	04	07	10	13	16	19	22
Line width (nm)	130	90	65	45	32	22	16	11
LWR (nm)					2.2	1.6	1.1	0.8

Lithography Solution

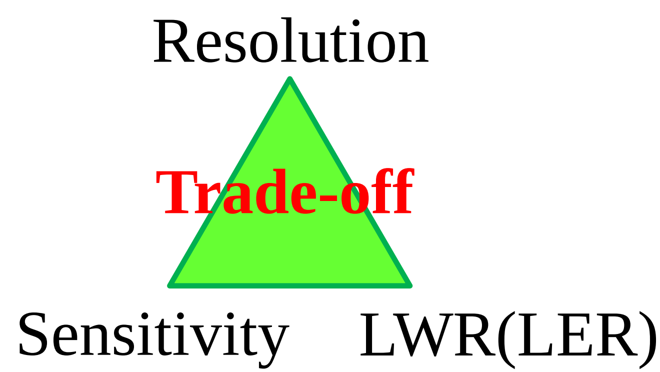
- KrF excimer (248 nm)
- ArF excimer (193 nm)
- ArF excimer Immersion (+DP)
- EUV (13.5 nm)
- EB for mask production

Two keywords in the development of resist materials and processes

Transition of basic science for material design



Trade-off relationships between resolution, sensitivity, and LER



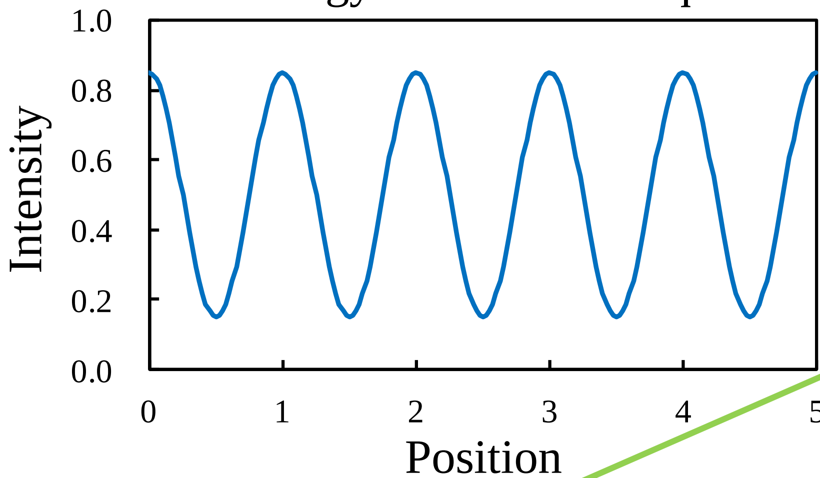
Chemically amplified resist

Typical components: Polymer, Acid generator, Quencher

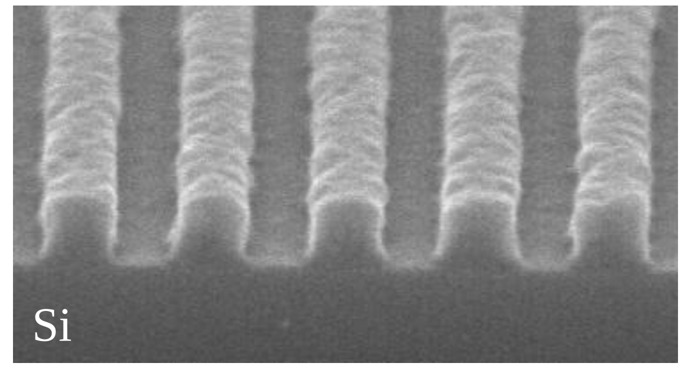
Role: Conversion of energy modulation to binary image

Exposure source

Energy modulation of quantum beam



Resist image



SEM image of resist

Photon/electron interaction with matter

Energy deposition → **Formation of acid image** → (Thermal energy) → **Formation of latent image** → **Development**

Decomposition of acid generator

Solubility change through chemical reaction

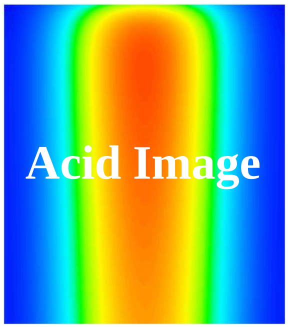
Acid diffusion, deprotection

Dissolution of molecules

Relationship between LER and chemical gradient

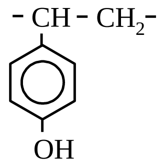
Aerial image

EUV

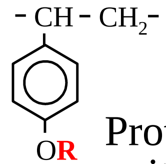


Cross section

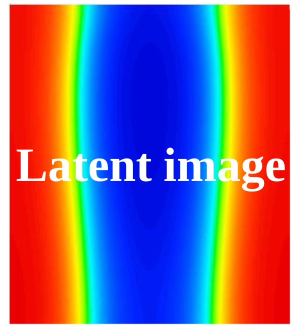
Soluble ← Can be controlled



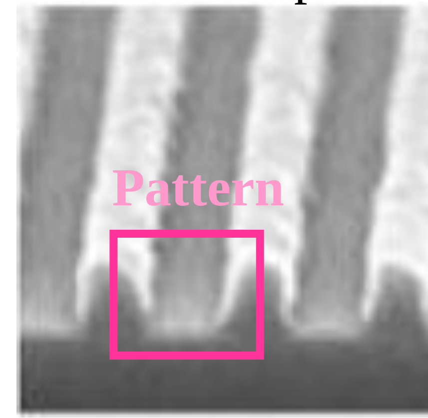
Insoluble

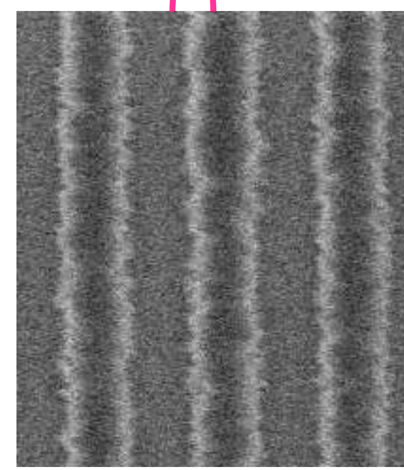


Protected unit



After development

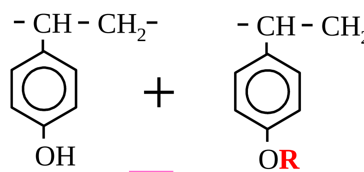




Top-down view

Mixture of soluble and insoluble molecules

Absolutely stochastic
Can not be controlled



(Spatially) partially soluble

LER formation

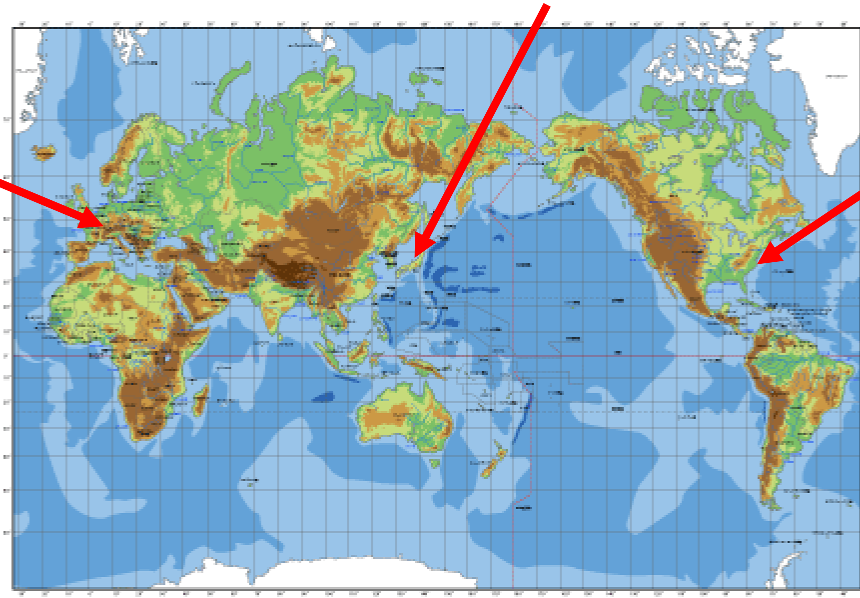
LER ∝ width of intermediate region ≒ $\dfrac{1}{\text{Chemical gradient}}$ ➡ $LER \approx \dfrac{f_{LER}}{dm/dx}$

Resist screening

Selete (later EIDEC)

IMEC

Sematech



IMEC, Sematech, and Selete (EIDEC) have supported the development of EUV lithography including resist material and processes.

A large number of resist materials have been tested in these sites.

Resolution

Sensitivity LWR(LER)

Evaluation of resist performance is tricky because of the trade-off relationship.

Performance (efficiency) of resist

The number of incident photons is limited because of the sensitivity requirement.

①How many photons can be absorbed?

Absorption coefficient: ~4 /µm

②How many acids can be generated by a single photon?

Quantum efficiency: 2-3

③How many dissolution inhibitor (protecting group) can be removed by a single acid during the diffusion of unit length?

Effective reaction radius

④How smoothly are the polymers dissolved in developer?

Relationship between LER and chemical gradient, f_{LER}

$$LER \approx \frac{f_{LER}}{dm/dx}$$

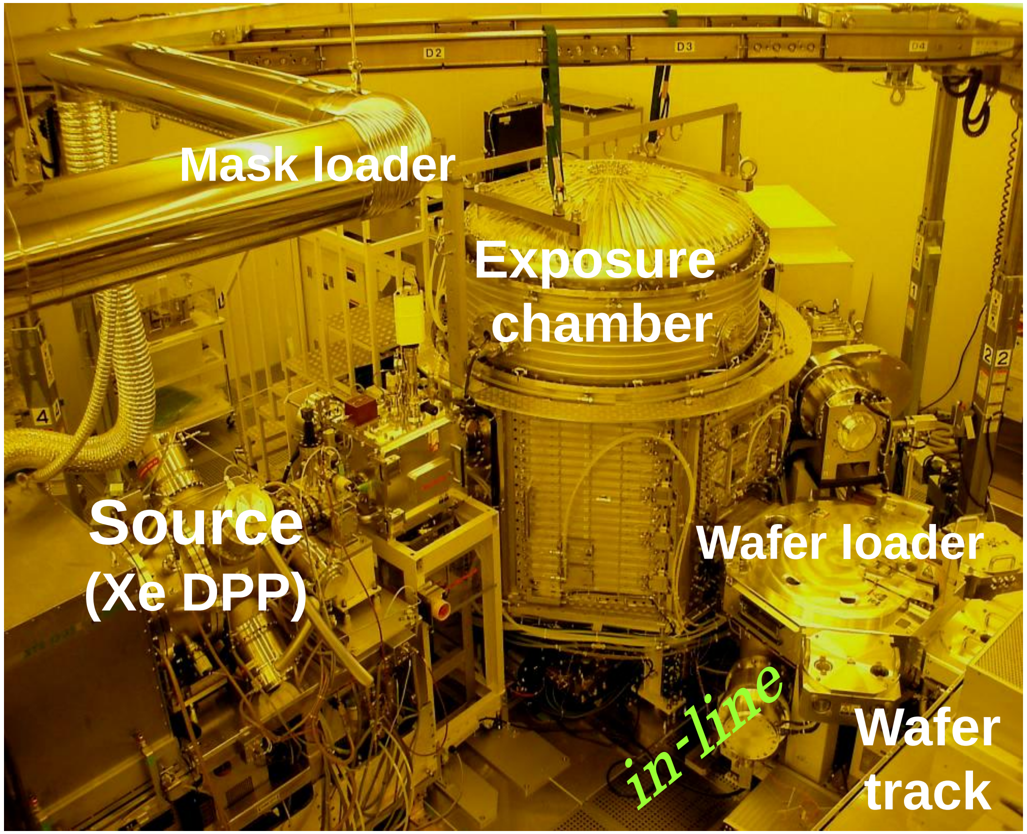
The chemical gradient is determined by ①−③

Generally, resists are evaluated using resolution, LER, and sensitivity.

We in collaboration with Selete evaluated the effective reaction radius and f_{LER} to understand the current status of chemically amplified resists.

Resist screening at Selete (EIDEC)

Small Field Exposure Tool : SFET

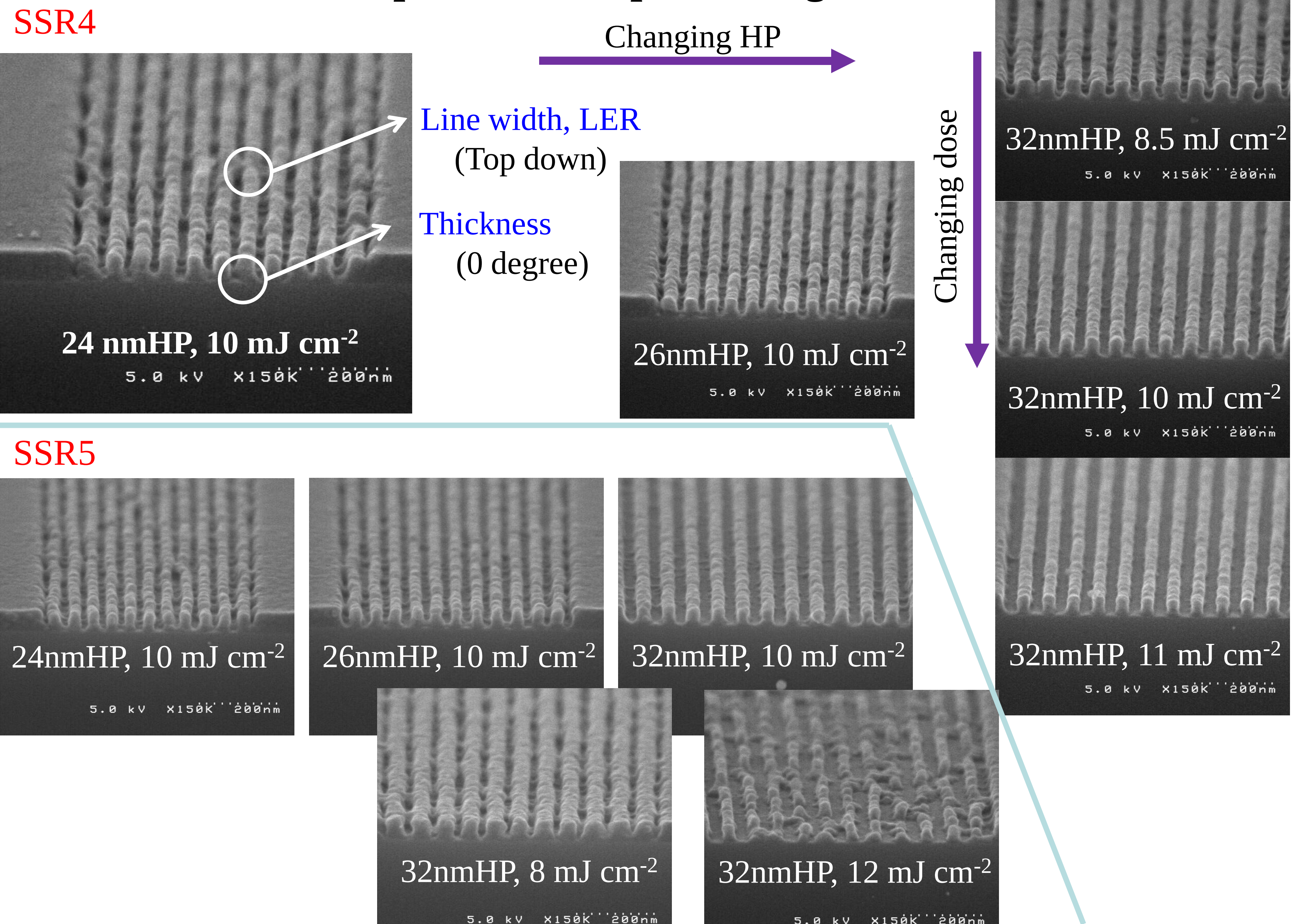


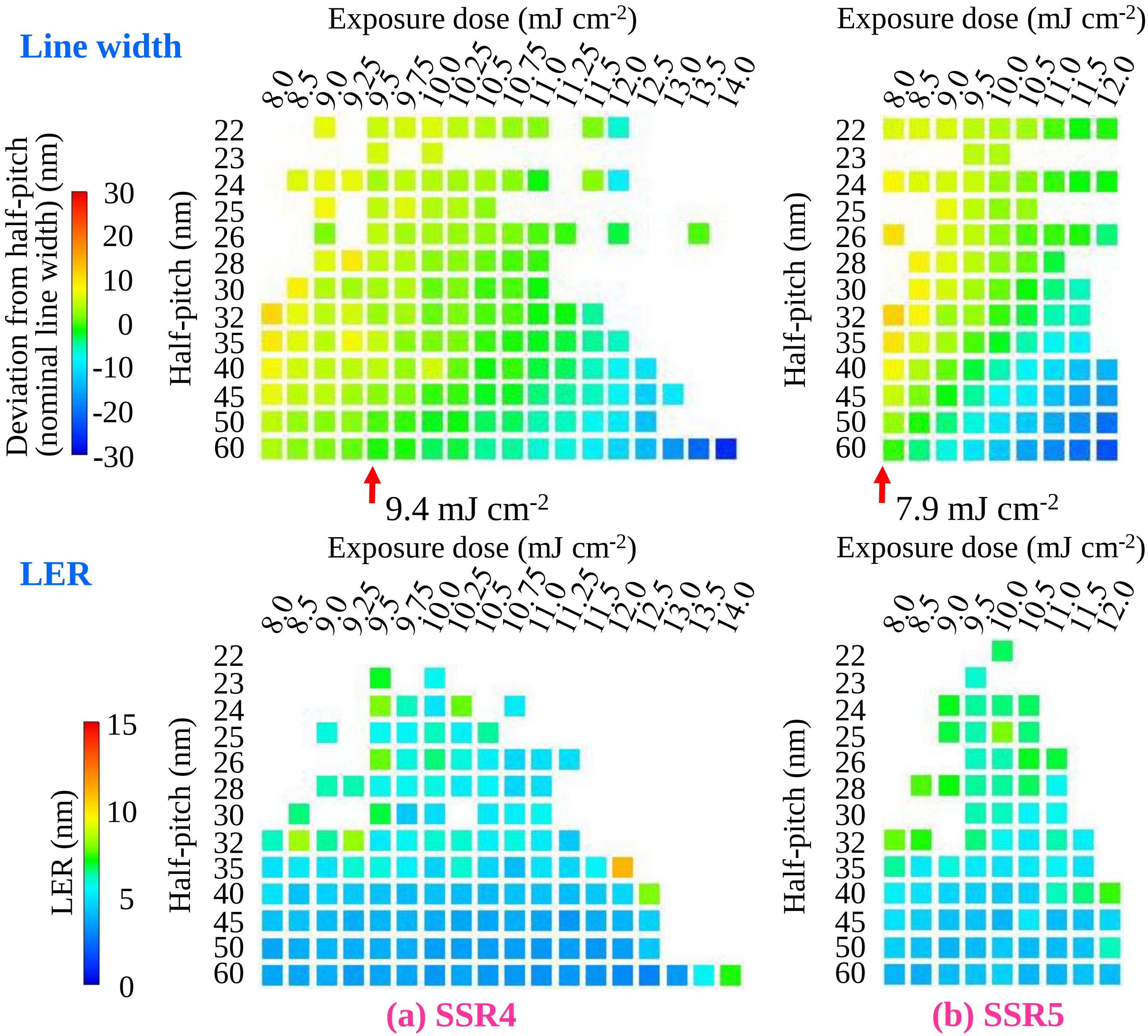
Items	Target Specifications
NA	0.3
Illumination mode	Annular(0.3/0.7), x-slit
Field size	0.2 x 0.6 mm
Magnification	1/5
Wavefront error	＜0.9 nm rms
Flare	＜7%（MSFR）
Source power	0.5W @IF
Wafer size	300 mm

Selete has reported highest performance resists among those tested using SFET as

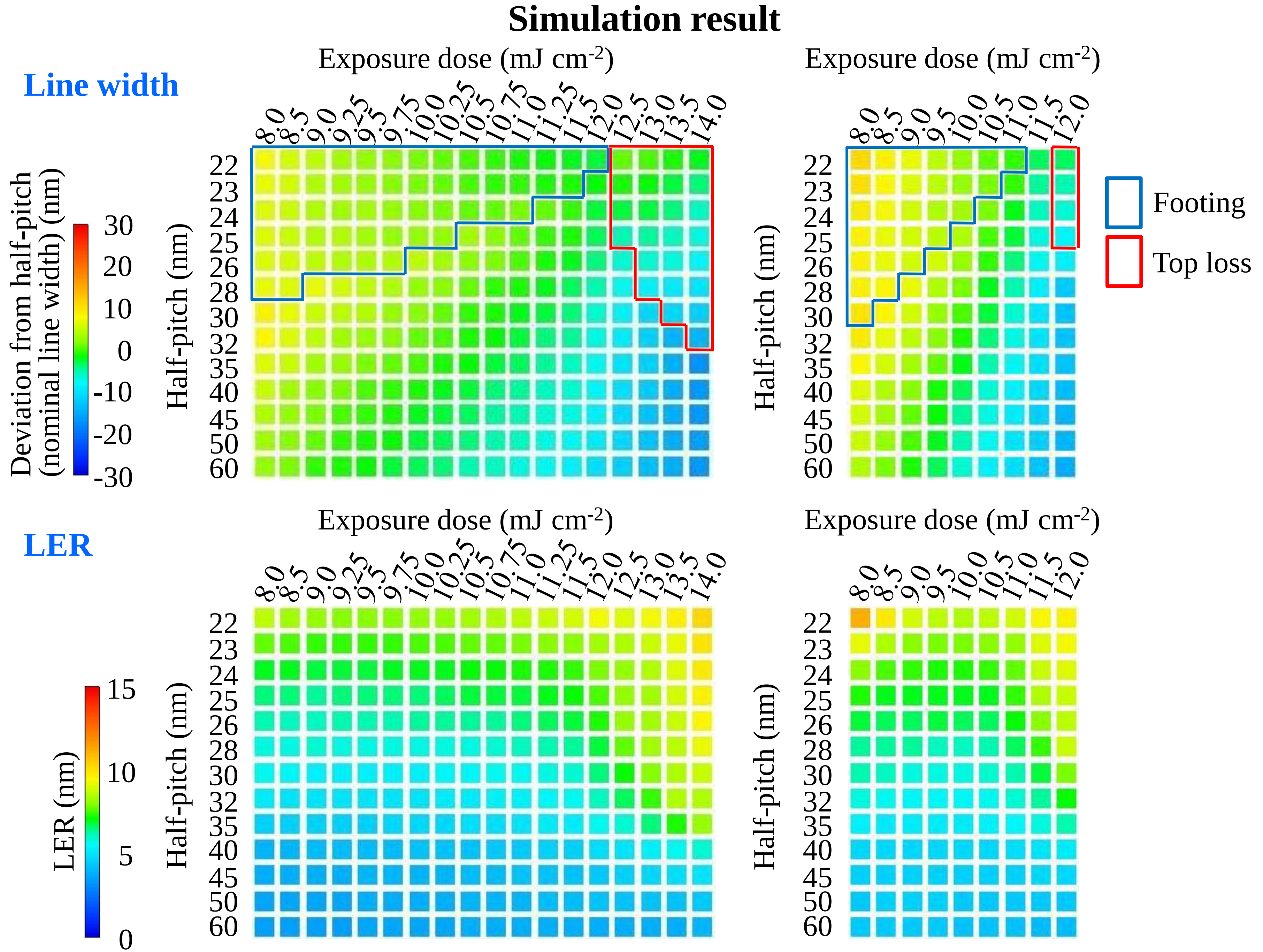
Selete Standard Resists (SSR1 to SSR7)

Representative patterning results





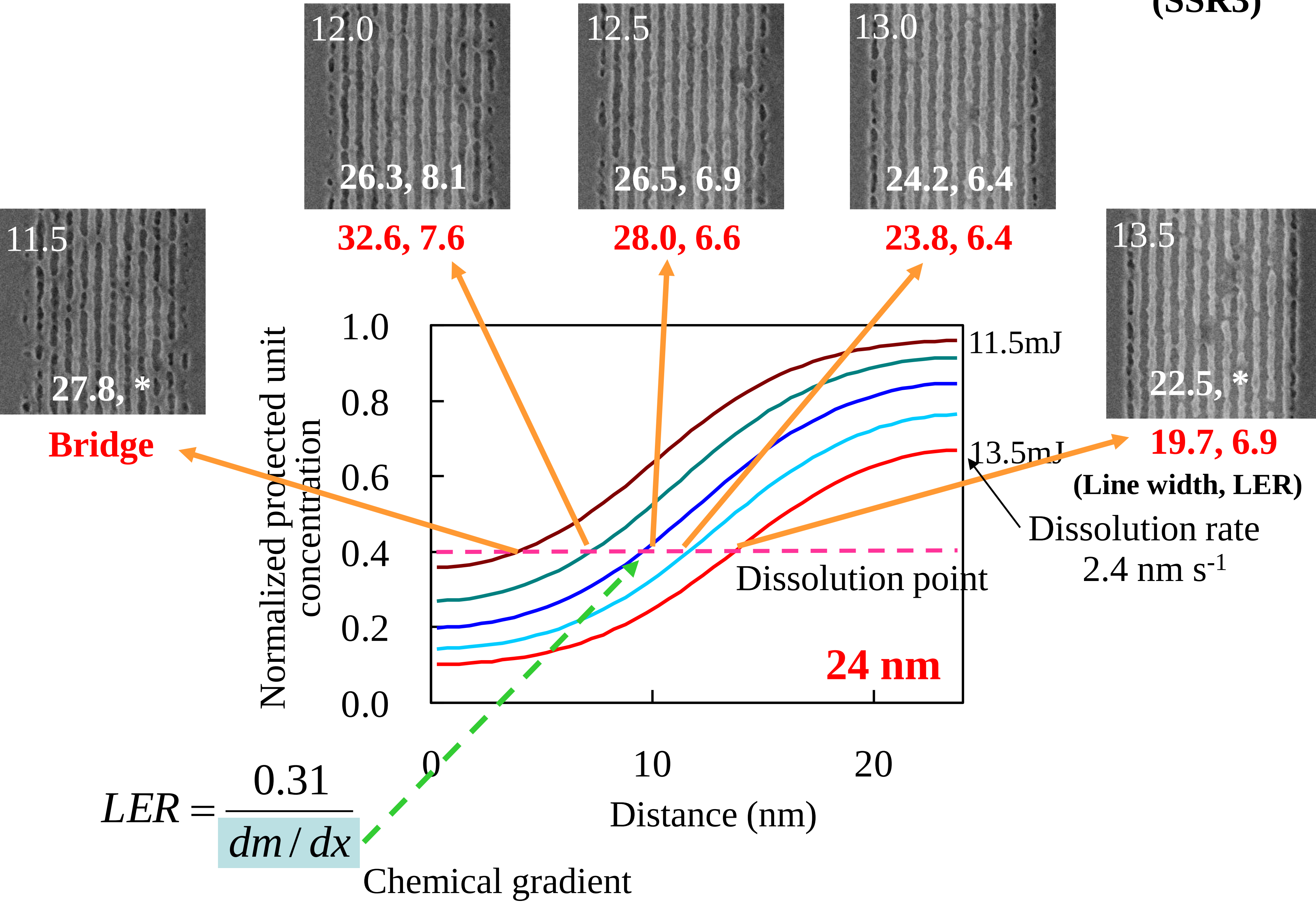
Line width
LER
Exposure dose (mJ cm-2)
Half-pitch (nm)
Deviation from half-pitch (nominal line width) (nm)
LER (nm)
9.4 mJ cm-2
7.9 mJ cm-2
(a) SSR4
(b) SSR5



Simulation result
Line width
Exposure dose (mJ cm-2)
8.0 8.5 9.0 9.25 9.5 9.75 10.0 10.25 10.5 10.75 11.0 11.25 11.5 12.0 12.5 13.0 13.5 14.0
8.0 8.5 9.0 9.5 10.0 10.5 11.0 11.5 12.0
Half-pitch (nm)
22 23 24 25 26 28 30 32 35 40 45 50 60
Deviation from half-pitch (nominal line width) (nm)
30 20 10 0 -10 -20 -30
Footing
Top loss
LER
LER (nm)
15 10 5 0

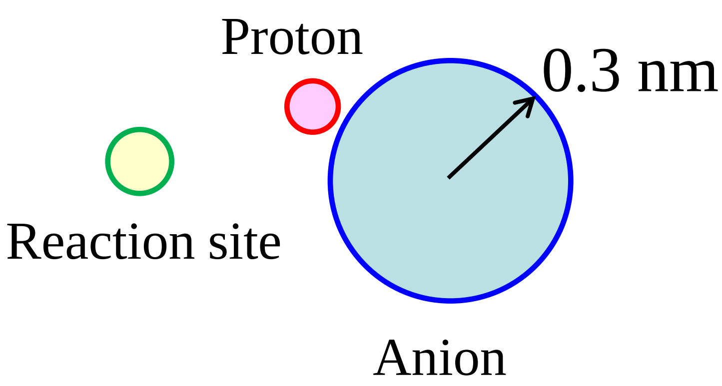
(a) SSR4 (b) SSR5

Reconstruction of latent images from does-pitch matrices of line width and LER (SSR3)

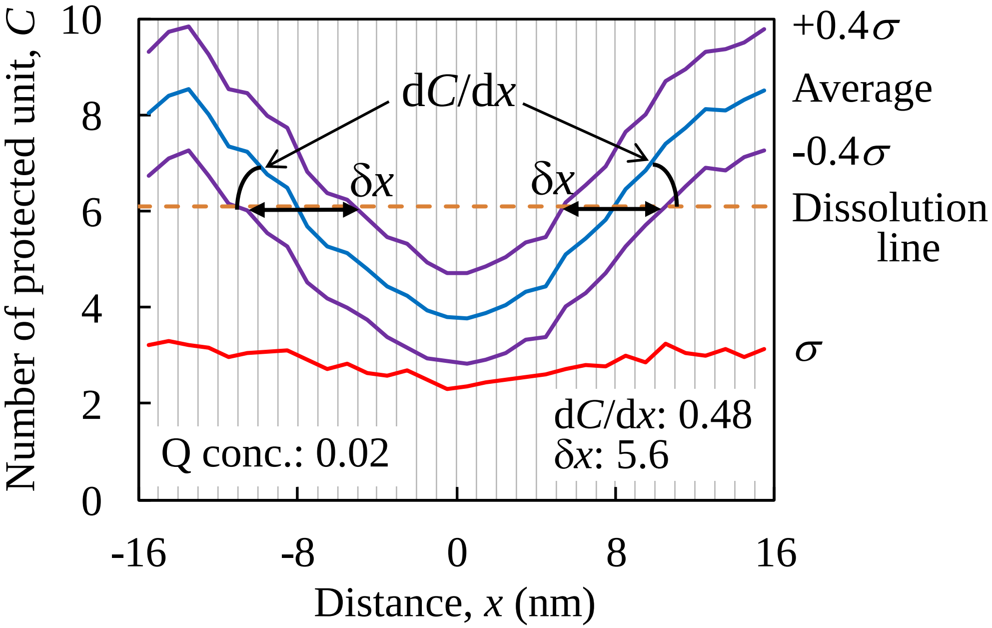


Evaluated parameters

Resist	Matrix	Effective reaction radius (nm)	f_{LER}
SSR3	Polymer	0.1	0.24-0.31
SSR4	Polymer	0.08-0.1	0.17-0.24
SSR5	Polymer	0.09	0.20
SSR7	Fullerene	0.06	0.14



Chemical reaction

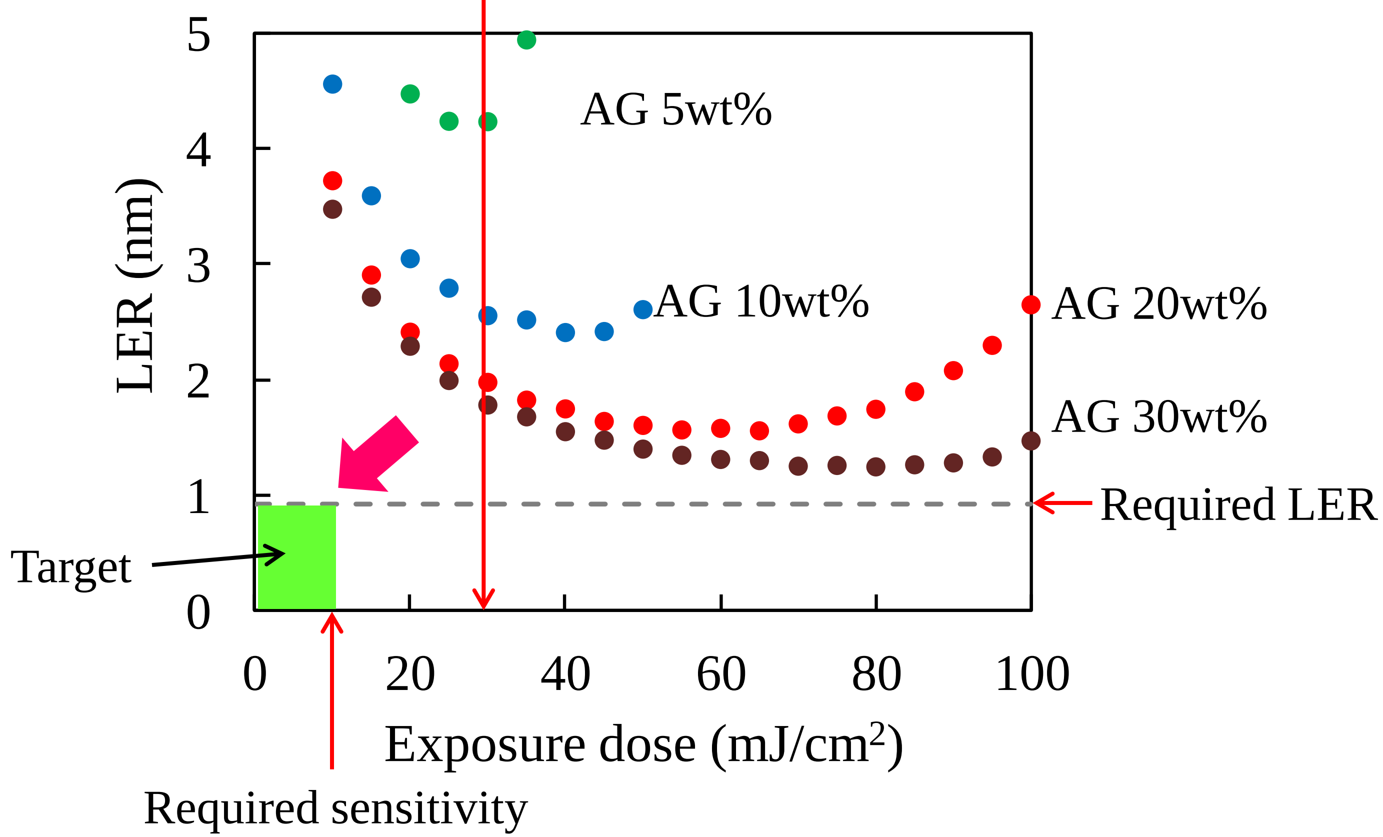


LER

Challenges

Half-pitch: **16 nm**
Optical contrast: 0.8
Eff. reaction radius: 0.1 nm
f_{LER}: 0.2

15 nm features has been reported to be resolved with 30 mJ/cm^2 sensitivity.



Absorption coefficient: Sum of absorption cross section of atoms
Quantum efficiency: Acid generator concentration
Effective reaction radius: Activation energies for deprotection and diffusion

Summary (1)

We have investigated resist patterns fabricated using an EUV exposure tool on the basis of reaction mechanisms. To simultaneously meet the requirements of resolution, LER, and sensitivity, it is essential to enhance the absorption coefficient of the resist, the quantum efficiency of acids, and the effective reaction radius of catalytic chain reaction. Especially, the absorption enhancement is the most important factor. Actually, it is not difficult to increase the absorption coefficient of the polymer, because the absorption coefficient against EUV is determined, not by chemical bonds but the photoabsorption cross sections of atomic elements. The problem is that the introduction of new atomic elements to the polymer significantly changes the chemistry induced in the resist films. It is not an easy task to increase the effective reaction radius of chemical reactions in the new resist platform to the same level as that in well-studied organic resist polymers.

Anion bound resist

It has been considered that the acid diffusion is the most serious problem for the improvement of resist performance in terms of **trade-off relationship**.

Recently, a chemically amplified resist with **anion-bound acid generator** attracted much attention.

Promising material for 16 nm node and beyond

↓

Reaction mechanism is unknown.

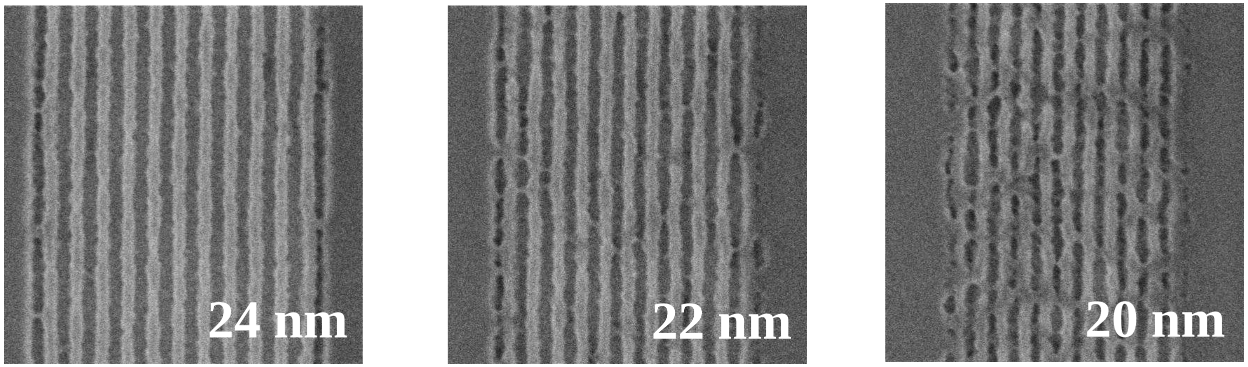
↓

An acid diffusion model in a chemically amplified resist with anion-bound acid generator

New simulation code was developed on the basis of **radiation chemistry**.

For the development of resist materials, particularly, used in the 16 nm node and beyond, it is important to understand the reaction mechanism of catalytic reactions induced in the anion-bound resists.

Basic idea



Anion-bound resist

SFET
Annular
18.16 mJ cm^{-2}

Similar sensitivity to that of blend type resists

➡ The efficiency of acid catalytic reaction is not bad.

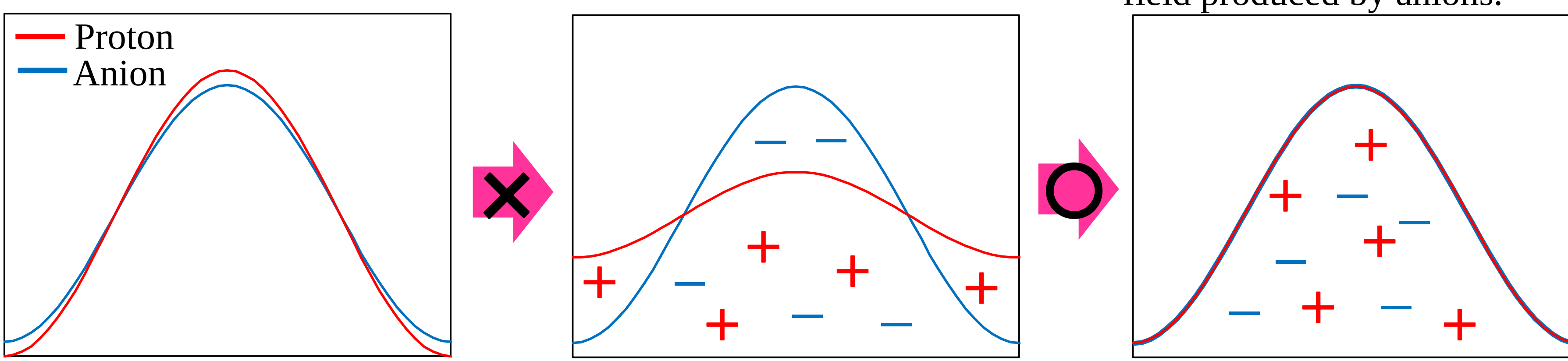
➡ Protons can diffuse. (Experimentally confirmed)

H. Yamamoto et al., Jpn. J. Appl. Phys. 43 (2004) L848.

High resolution

➡ Protons cannot diffuse freely.

Protons diffuse under the electric field produced by anions.



Initial distribution

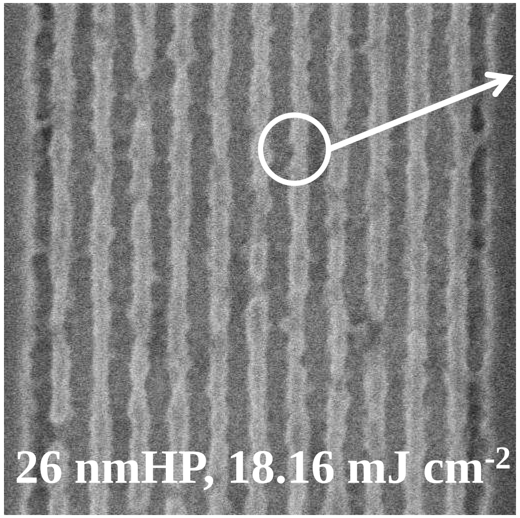
PEB

PEB

Proton diffusion model

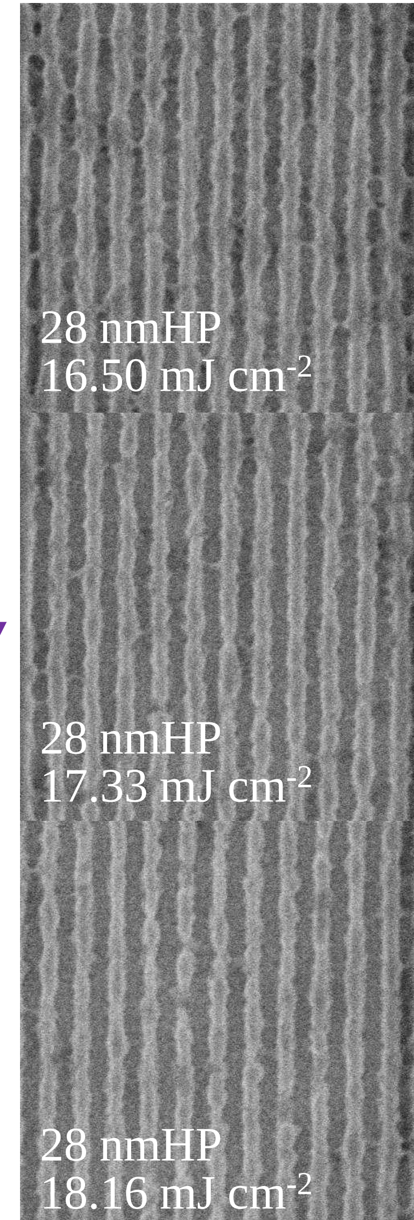
Representative patterning results

Chemically amplified resist with anion-bound AG

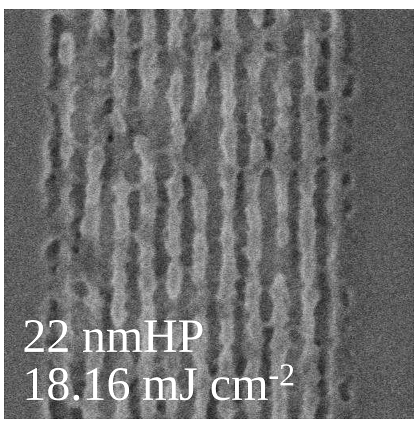


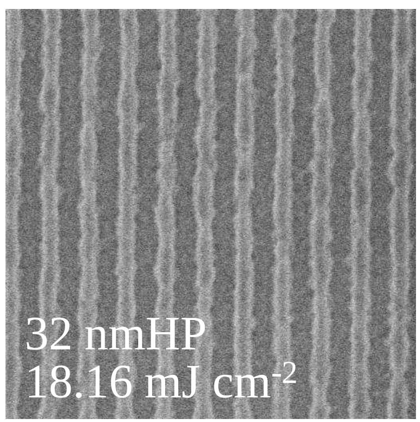
Line width, LER

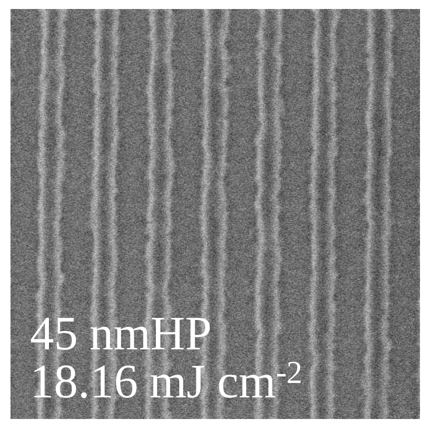
Changing exposure dose



Changing HP



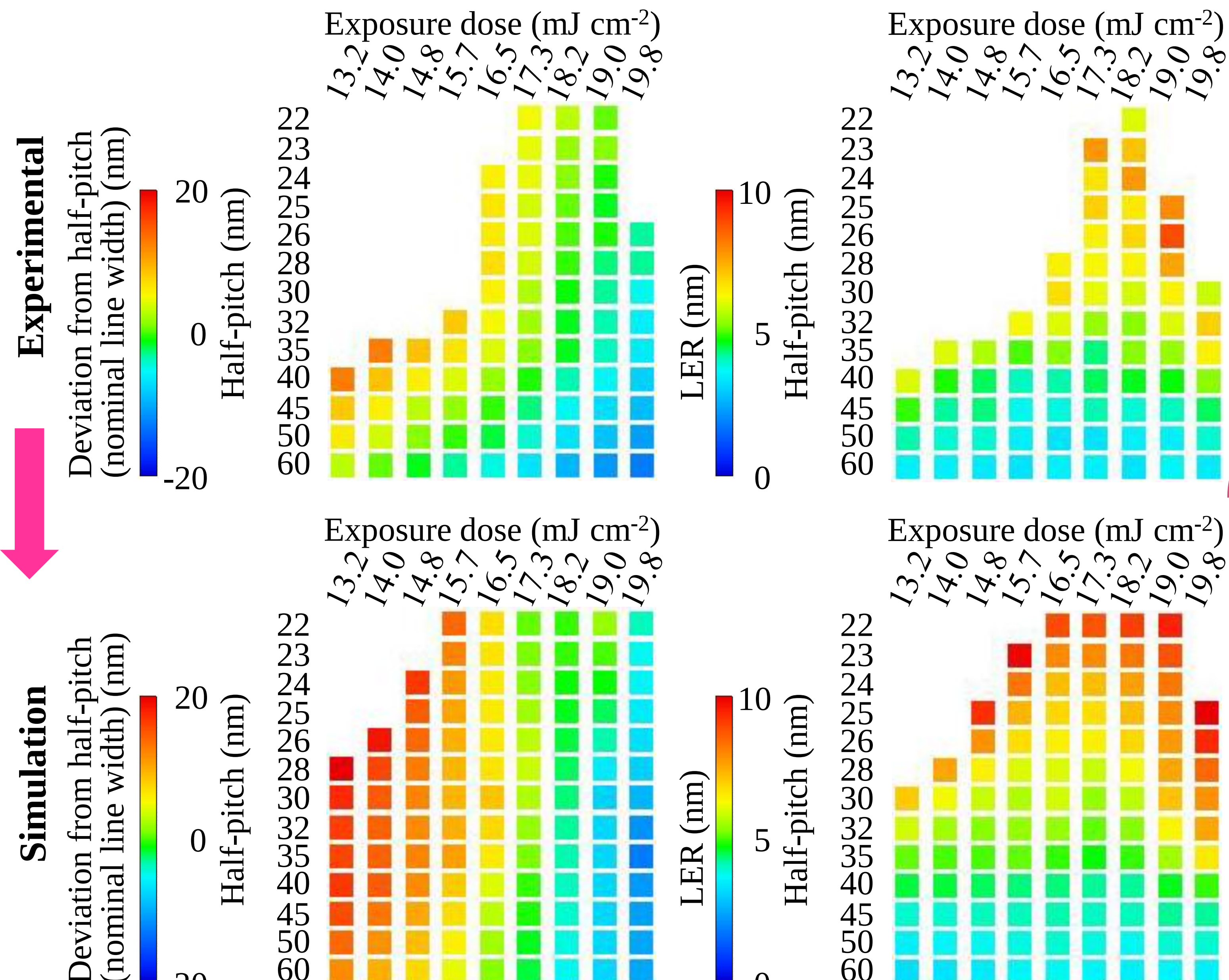




Conventional dose-pitch analysis

Relationship between LER and chemical gradient

Analysis of dose-pitch matrices of anion-bound resist



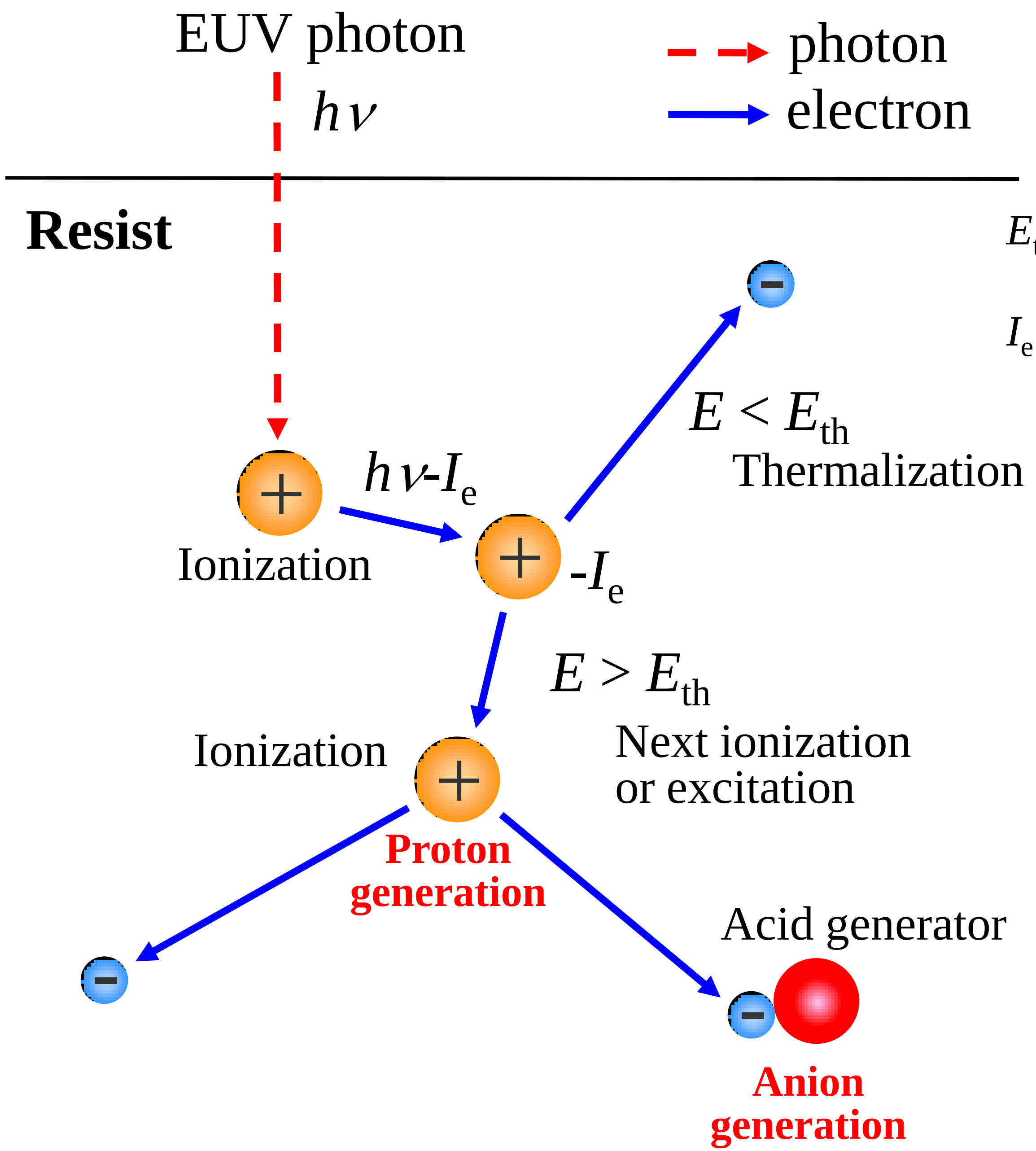
(a) Line width

(b) LER

$$LER = \frac{0.20}{dm/dx}$$

m: normalized protected unit concentration

Sensitization mechanism of EUV resists



E_{th}: Threshold energy for electronic excitation

I_e: Ionization energy

Simulation processes

(1) Absorption

(2) Deceleration

$E_{th} < E < h\nu$-I_e

(3) Deceleration

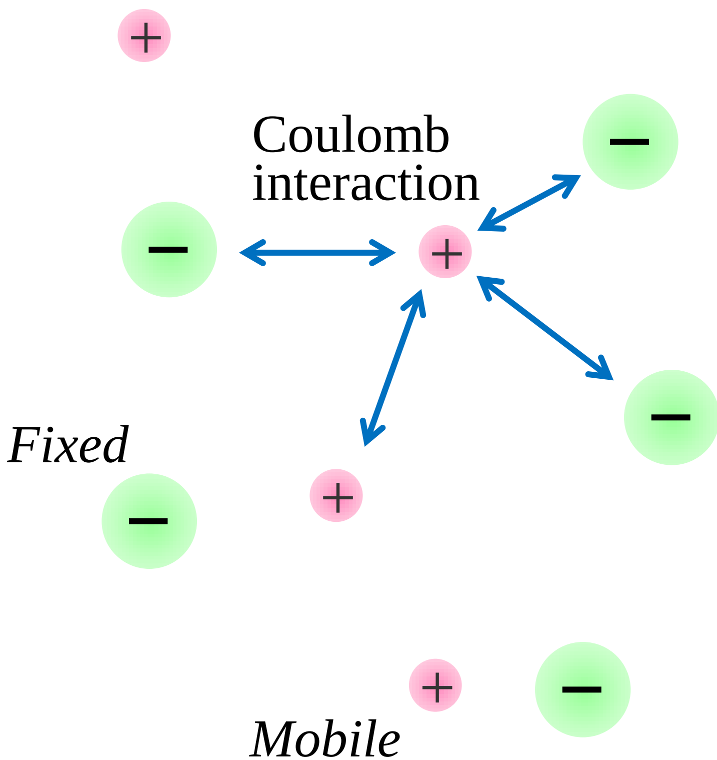
25 meV $< E < E_{th}$

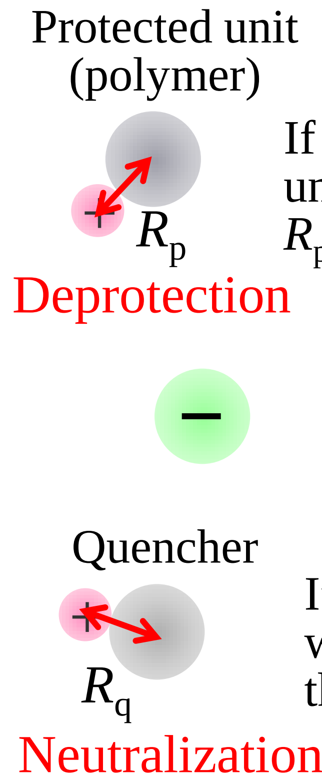
(4) Electron diffusion and reaction

E=25 meV

Post exposure baking (PEB)

Simulation of proton diffusion and deprotection





If a proton reaches a protected unit within the reaction radius, R_p, the deprotection is induced.

If a proton reaches a quencher within the reaction radius, R_q, the proton is neutralized.

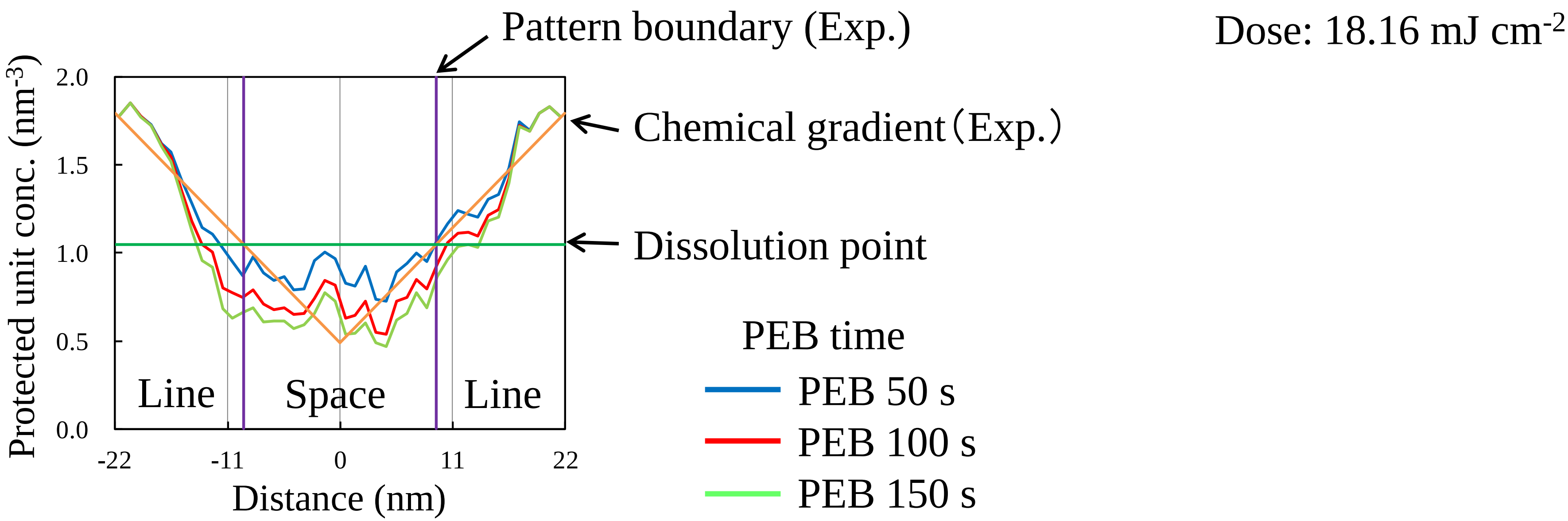
Immediately after exposure, protons are separated from anions because of their different origins.

Monte Carlo simulation

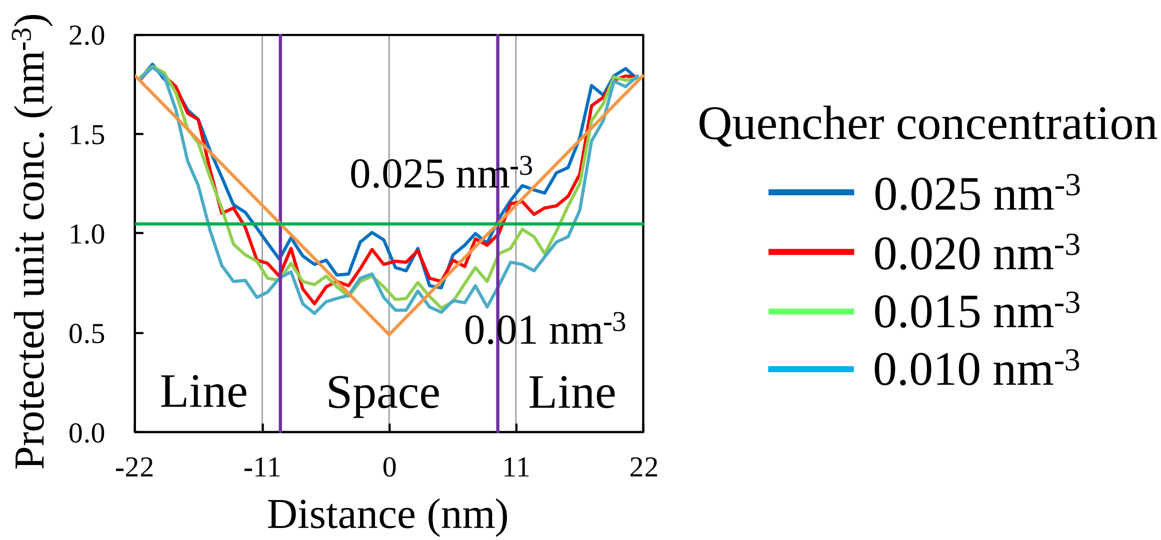
Electric field

$$\underbrace{\delta \mathbf{r}}_{\text{Displacement of proton}} = \frac{eD\mathbf{E}}{kT}\delta t + \sqrt{6D\delta t}\,\underbrace{\mathbf{n}}_{\text{Random vector}}$$

Comparison with SFET exposure (22 nm half-pitch)

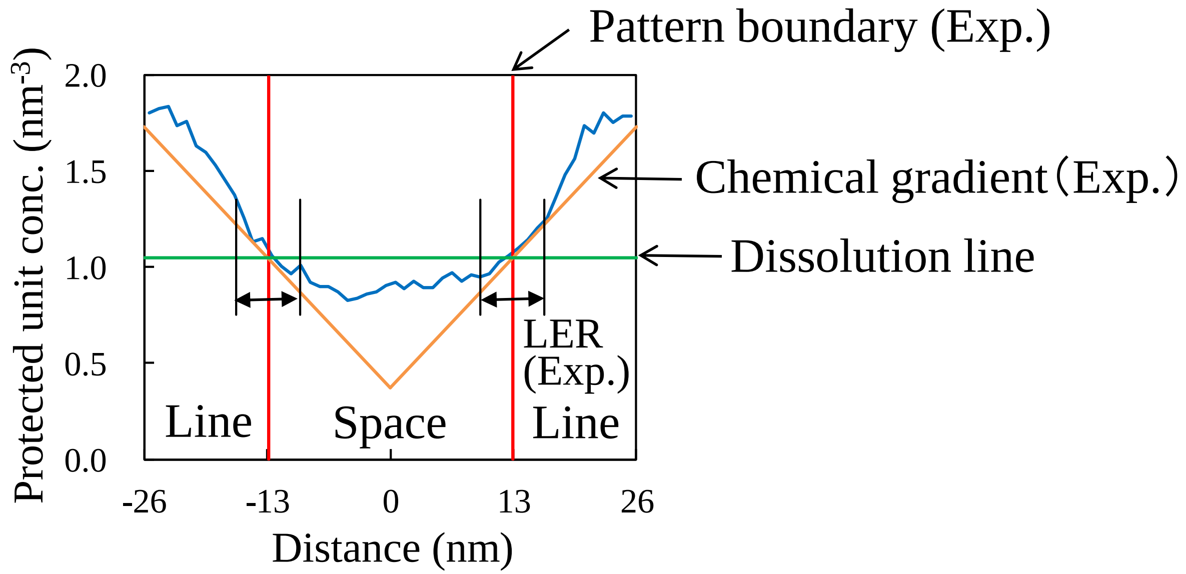


PEB time dependence

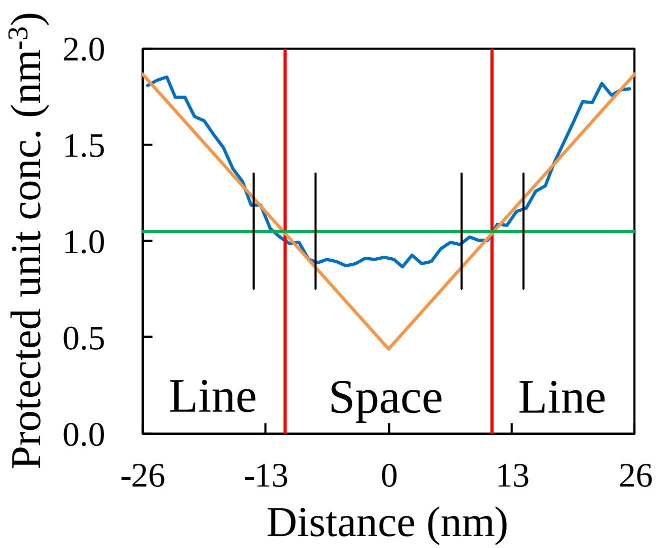


Quencher concentration dependence

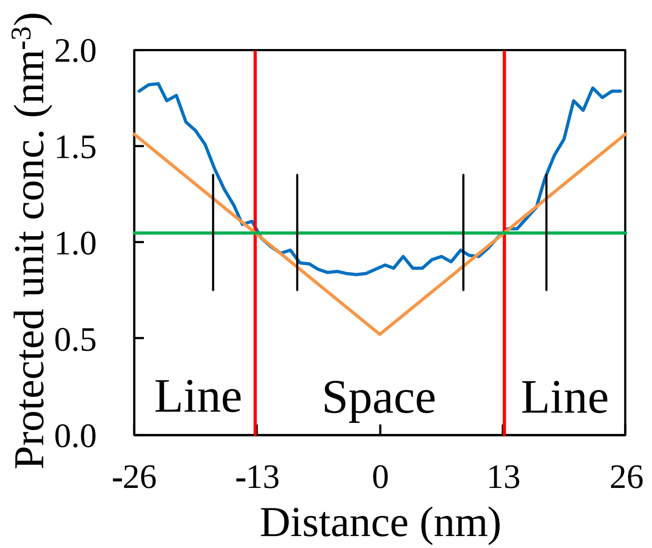
Dose dependence of latent image (26 nm half pitch)



Dose: 18.16 mJ cm^{-2}

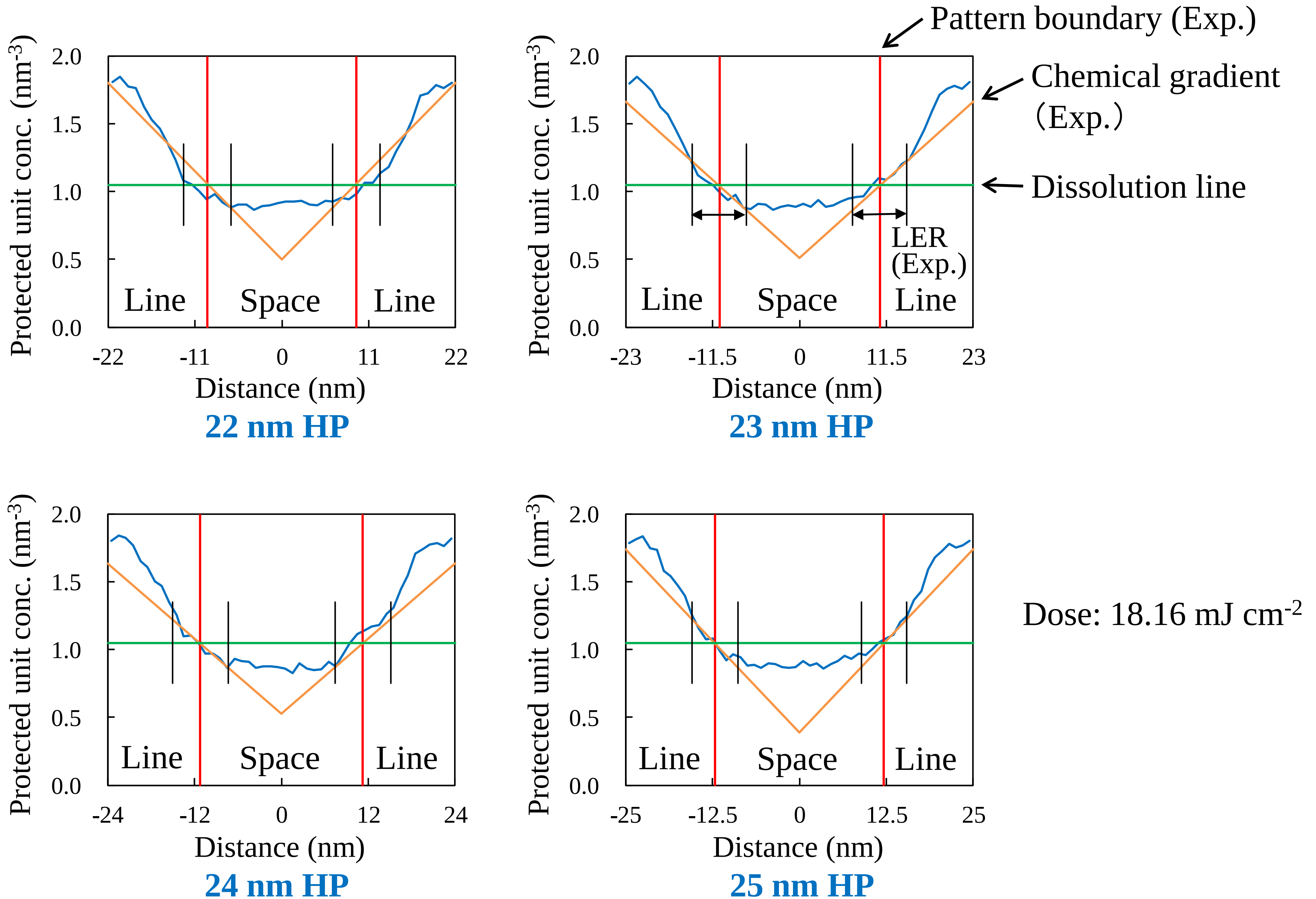


Dose: 17.33 mJ cm^{-2}



Dose: 18.99 mJ cm^{-2}

Half-pitch dependence of latent image



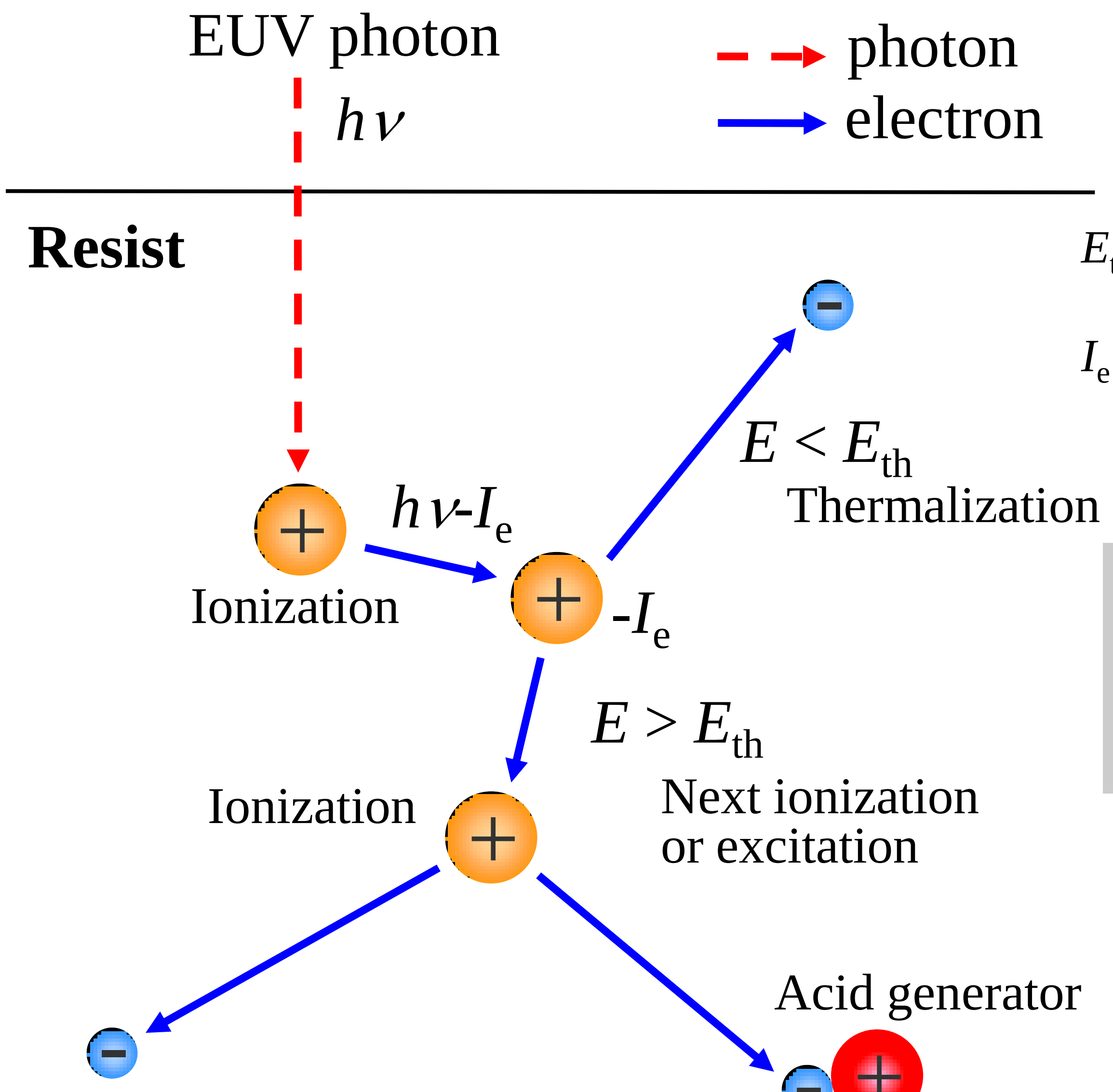
Summary (2)

The catalytic chain reaction induced in a chemically amplified resist with anion-bound AG was modeled. The calculated latent images were compared with the resist patterns fabricated using SFET of EIDEC. In the preliminary examination, the calculated images well agreed with the experimental results. The detailed analysis of resist patterns using the developed simulation code is ongoing to obtain the material design strategy for 16 nm node and beyond.

Acknowledgement

This work was partially supported by the New Energy and Industrial Technology Development Organization (NEDO).

Reduction of wavelength



E_{th}: Threshold energy for electronic excitation

I_e: Ionization energy

Simulation processes

(1) Absorption
(2) Deceleration

Wavelength dependent

$E_{th} < E < h\nu$-I_e

(3) Deceleration

25 meV $< E < E_{th}$

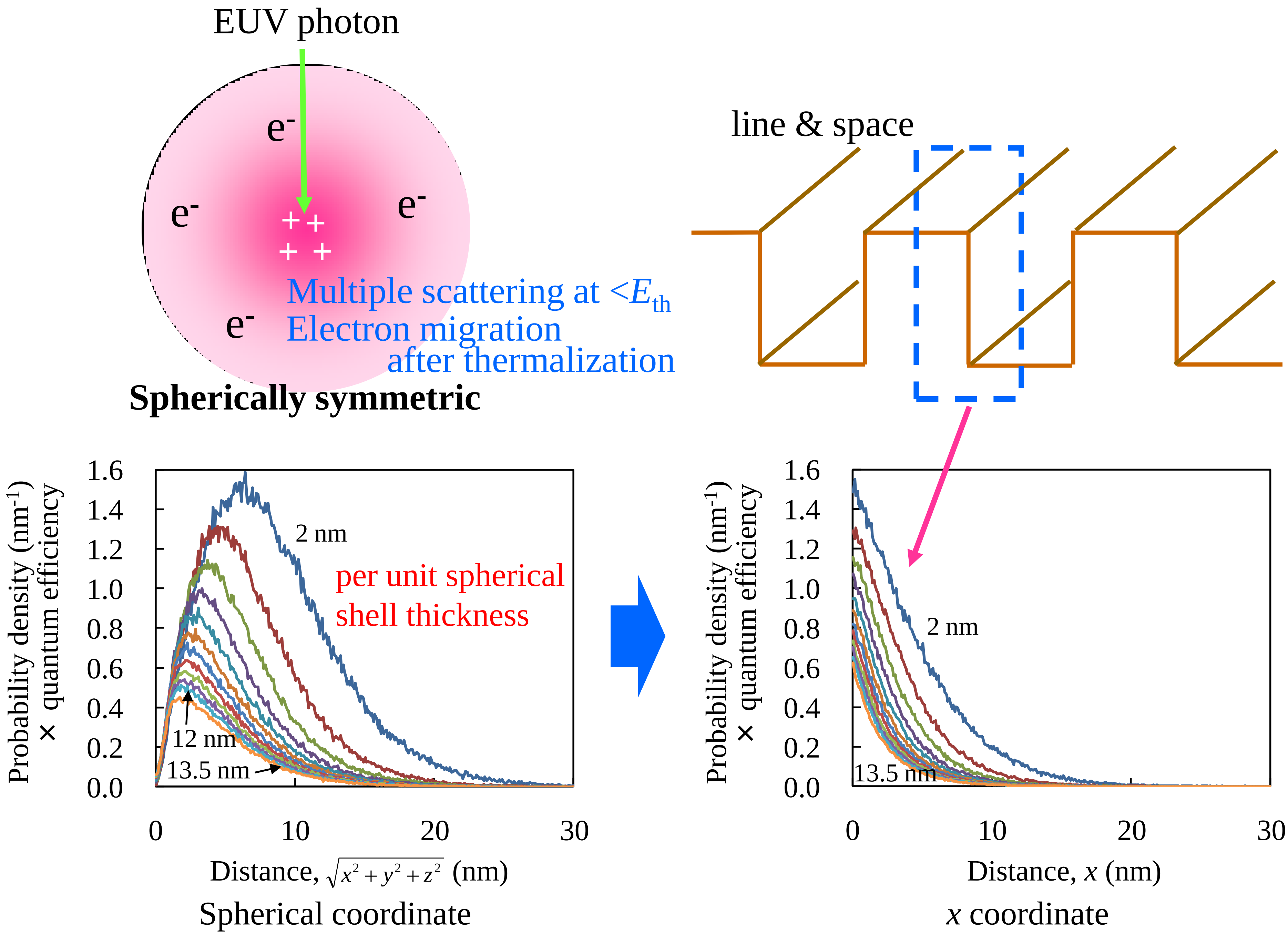
(4) Electron diffusion and reaction

E=25 meV

Activation energy for dissociative electron attachment : ~0

The electron with thermal energy can sensitize acid generators.

Wavelength dependence of resolution blur caused by secondary electrons



Performance of conventional chemically amplified resists –Resolution-

Acid image resolution (acid diffusion length does not depend on wavelength)

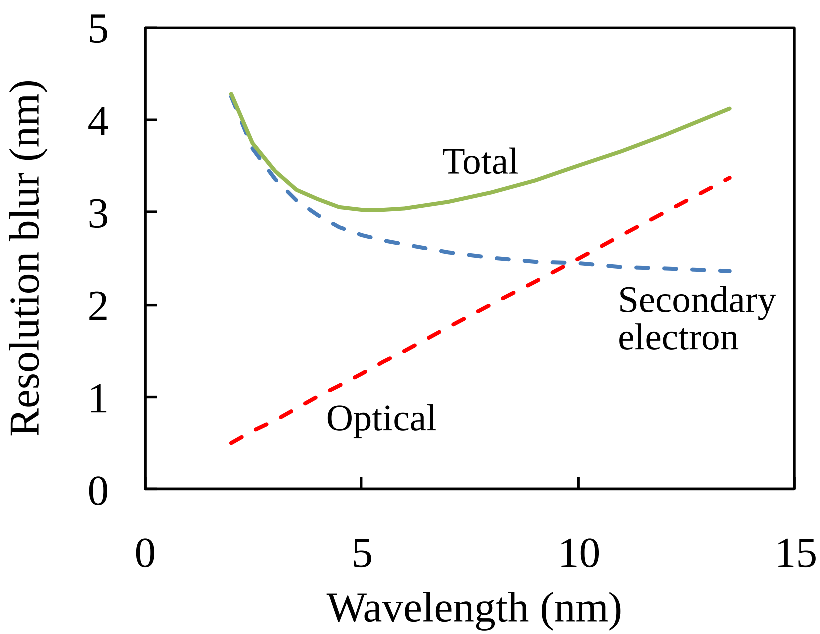
Optical blur, b_{optical}

$$b_{optical} = \frac{CD}{2} \qquad CD = k_1 \frac{\lambda}{NA}$$

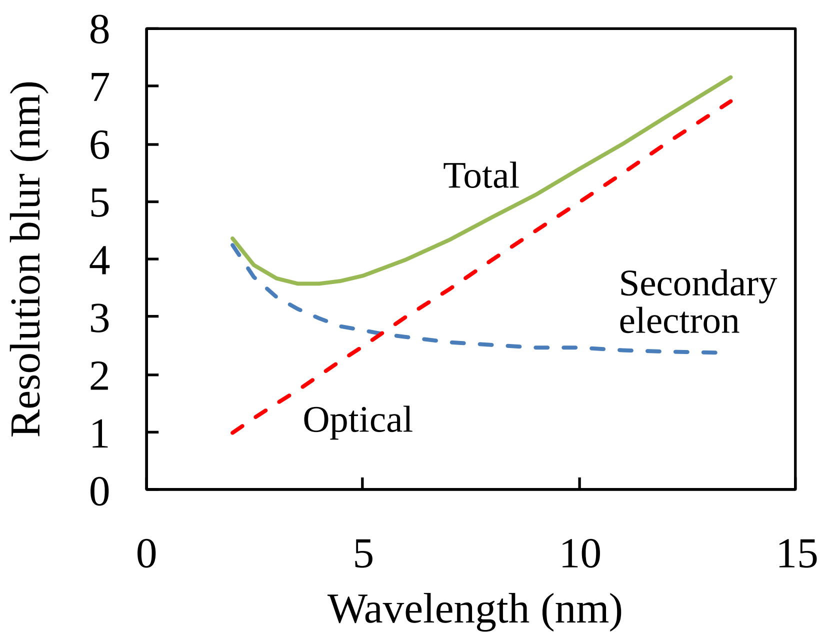
Secondary electron blur, b_{electron}

Average distance

Total blur, $$b_t = \sqrt{b_{optical}^2 + b_{electron}^2}$$



$$\frac{k_1}{NA} = 0.5$$



$$\frac{k_1}{NA} = 1$$

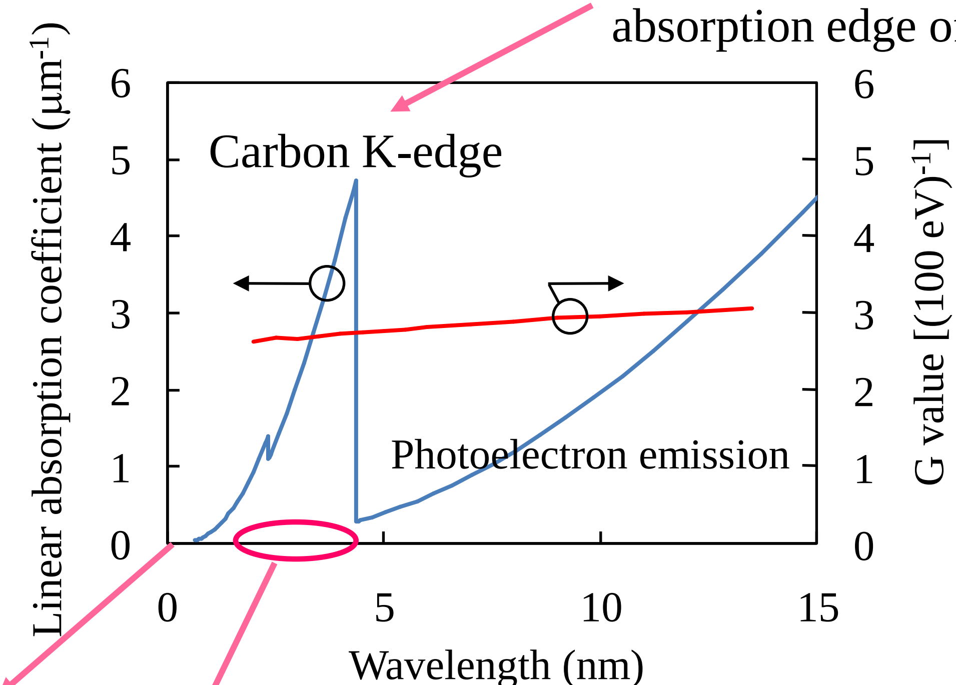
Performance of conventional chemically amplified resists –Sensitivity-

Acid concentration (acid diffusion length does not depend on wavelength)

Absorption coefficient

Acid generation efficiency per unit absorbed dose (G value)

The W-value increases by 10-20% at the absorption edge of the inner shell.



Compton scattering

Inner shell excitation

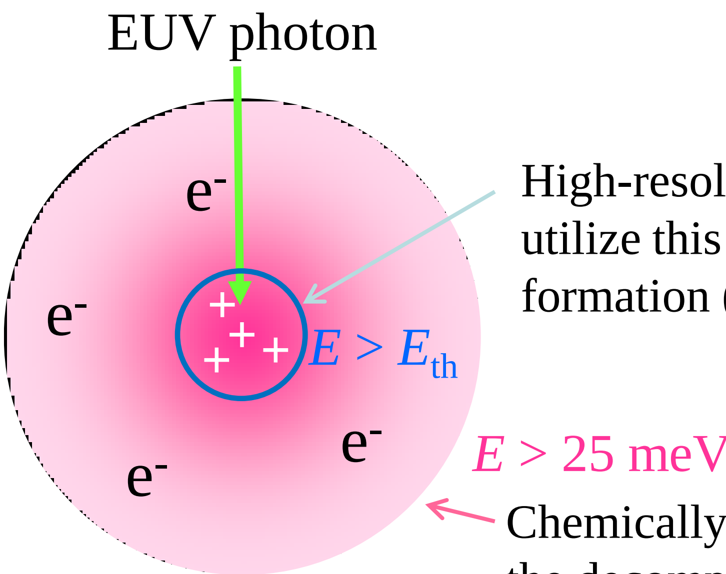
Auger electron (light element)

Positively affect resolution

Fluorescence X-rays (heavy element)

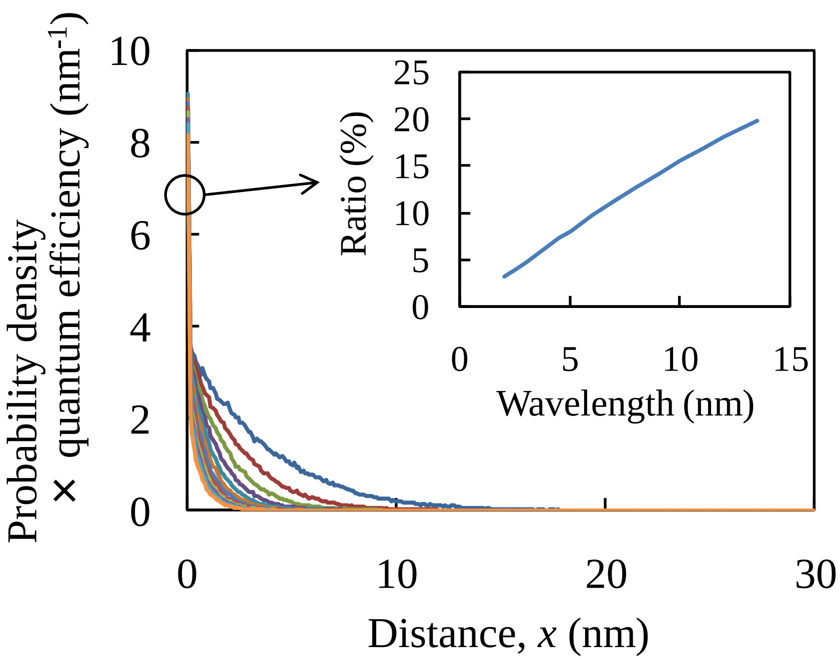
Negatively affect resolution

Non-chemically amplified resists

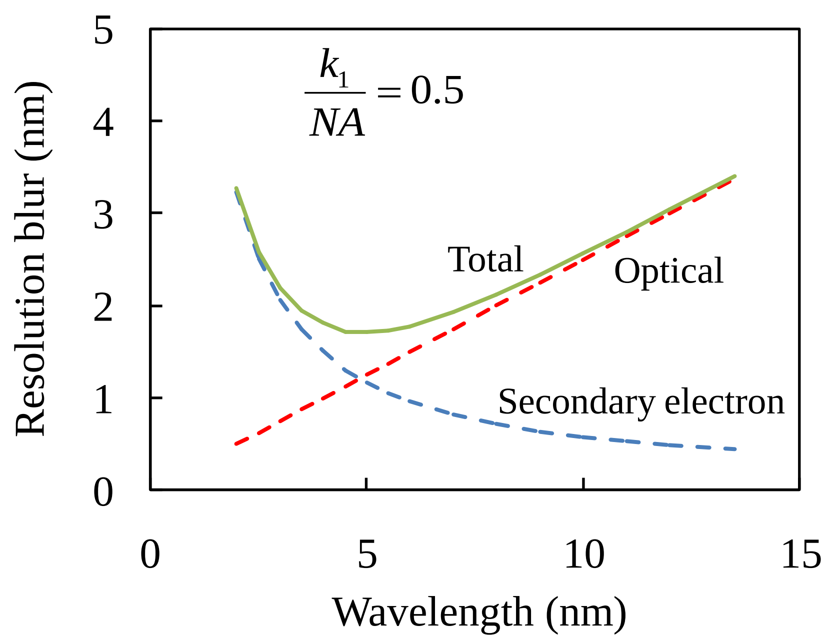


High-resolution conventional resist such as PMMA utilize this part for the chemical reaction for pattern formation (main chain scission).

Chemically amplified resists utilize this part for the decomposition of acid generators.



Distribution of radical cation



Resolution blur of L&S pattern

Summary (3)

The wavelength dependence of lithography resolution was investigated in the wavelength region of extreme ultraviolet. The resolution is expected to be highest at a wavelength of 3-5 nm, depending on NA of exposure tools. In the case of low-NA tools, the merit of wavelength reduction from 13.5 nm is significant. However, the merit of wavelength reduction is lost in the case of high-NA tools, particularly when the increase in transparency of the resist with the reduction in wavelength is taken into account. One of the keys to the realization of 6.67nm lithography is the development of high-absorption resists.

Acknowledgement

This work was partially supported by the New Energy and Industrial Technology Development Organization (NEDO).